

I. THE CATALYTIC DEHYDROGENATION
OF PIPERIDINE

II. THE REACTIONS OF MANNICH BASES WITH
INDOLE AND RELATED COMPOUNDS

BY

CAL YALE MEYERS

A.B., Cornell University, 1948
M.S., University of Illinois, 1949

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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I. THE CATALYTIC DEHYDROGENATION OF PIPERIDINE

INTRODUCTION

Since many pharmaceuticals and intermediates contain the pyridine nucleus, the synthesis of these compounds has been important. Useful synthetic methods involving the dehydrogenation of hydropyridines to pyridines are limited¹, and the present investigation was undertaken to formulate a good dehydrogenation scheme for the conversion of piperidines to pyridines.

DISCUSSION OF RESULTS

Piperidine was readily dehydrogenated to pyridine by pyrolysis over coconut charcoal catalyst. The maximum yields were in the range of 50 per cent; a portion of the piperidine was cleaved to ammonia and volatile hydrocarbons. No tarry material was formed in this process.

Metallic oxide catalysts tended to produce tarry products lowering considerably the yield of pyridine. Generally, no volatile liquid or ammonia was produced with these catalysts.

The "red color test"², involving the reaction of benzenesulfonyl chloride with pyridine in alkaline solution, was used advantageously in detecting small amounts of pyridine in pyridine-piperidine mixtures.

Since pyridine has distinctive peaks in the ultraviolet region³ and the optical density of each peak was found to be directly proportional to the concentration, the quantity of pyridine in each pyrolysate and hence, the per cent yield, was determined by a study of the ultraviolet absorption spectrum of the pyrolysate from each dehydrogenation.

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II. THE REACTIONS OF MANNICH BASES WITH INDOLE AND RELATED COMPOUNDS

INTRODUCTION

Butenandt and his associates¹ recently found that indole condensed with diethyl (1-piperidylmethyl)formamidomalonate (I) forming α -(1-piperidyl)skatole (II), diethyl (skatyl)-formamidomalonate (III) or a mixture of the two compounds depending upon the solvent and presence of a condensation agent.

The present study was initiated to determine the mechanism of this condensation and discover its scope and limitations.

DISCUSSION OF RESULTS

In the presence of a base, indole condensed with I producing III as the major product. In the absence of a condensation agent, the reaction proceeded with the formation of II and III, the yield of II decreasing and of III increasing with reaction time. Also in the absence of a condensation agent, II condensed with formamidomalonic ester producing III. The experimental data indicated that II is intermediary in the formation of III in the reaction under consideration.

In several instances the two products (II and III) combined physically producing a mixture which varied in composition but not in melting point, even after several recrystallizations. The mixture was resolved into its components by fractional crystallization from petroleum ether.

The condensation under discussion was not general, acetophenone, malonic ester, pyrrole and imidazole failing to condense with I. β -Naphthol, however, did react producing α -(1-piperidylmethyl)- β -naphthol along with another crystalline solid.

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VITA

Cal Yale Meyers was born on November 14, 1927, in Utica, New York, where he received his public school education. Following graduation from the Utica Free Academy in June, 1945, he entered Cornell University from which institution he received the Bachelor of Arts degree in August, 1948. In September of that year he entered the Graduate College of the University of Illinois and received the Master of Science degree in August, 1949. He held a Special Research Assistantship from 1948 to 1950 and a Teaching Assistantship during the academic year 1950-51.



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